

# Takovite–Aluminosilicate–Cr Materials Prepared by Adsorption of $\text{Cr}^{3+}$ from Industrial Effluents As Catalysts for Hydrocarbon Oxidation Reactions

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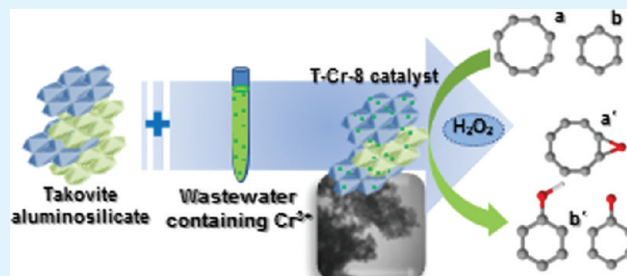
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**ABSTRACT:** The catalytic efficiency of takovite–aluminosilicate–chromium catalysts obtained by adsorption of  $\text{Cr}^{3+}$  ions from aqueous solutions by a takovite–aluminosilicate nanocomposite adsorbent is reported. The adsorbent was synthesized by the coprecipitation method. The catalytic activity of the final Cr–catalysts depended on the amount of adsorbed chromium. (Z)-cyclooctene conversion up to 90% with total selectivity for the epoxide was achieved when the oxidation was carried out with hydrogen peroxide, at room temperature. After five consecutive runs, the catalysts maintained high activity, although after the sixth reuse, the epoxide yields strongly decreased to 35%. The catalysts were also efficient for cyclohexane oxidation, reaching up to 18% conversion, with cyclohexanone/cyclohexanol selectivity close to 1.2. On the whole, their use as catalysts gives a very interesting application for the solids obtained by adsorption of a contaminant cation such as  $\text{Cr}^{3+}$ .

**KEYWORDS:** takovite–aluminosilicate nanocomposite, chromium, adsorption, catalytic oxidation



## 1. INTRODUCTION

Some heavy metals are micronutrients; living organisms usually store and transport them in small amounts (oligoelements) to ensure their presence at appropriate concentrations for the formation of metalloproteins or cofactors.<sup>1,2</sup> Well-known examples are the heme groups, chlorophyll, and cytochromes. However, these metals become toxic over a certain concentration. In fact, contamination of water by heavy metals is a matter of major concern. There is increased awareness of the potentially hazardous effects of elevated metal levels in the environment. For instance, Pb(II), Cr(VI), Hg(II), Cd(II), and Ni(II), which are found in the aqueous waste streams of industrial plants such as metal plating, mining industries, and tanneries, have become prominent pollutants nowadays. They result in potentially toxic or lethal effects because they are not biodegradable and tend to accumulate in living organisms, thereby causing various diseases and disorders.<sup>3</sup>

Chromium is one of the heavy metals that deserves the most attention, especially in developing countries. This is mainly because of its application in leather processing, although it can also be generated by other production plants like textile, electroplating, and metal finishing industries, as well as varnish

and wood preservation.<sup>4,5</sup> Leather tanning is the multi-step process through which raw hides or skins are converted into leather.<sup>6</sup>

One of the tanning methods proceeds via formation of chromium cross-linkage with collagen chains. This provides the biochemical stabilization of the dermal substance, thereby minimizing protein decomposition and maximizing hydrothermal stability. Stabilization improves the resistance of the proteins in the skin/hide against wet heat, dry heat, and thermomechanical stress. The use of chromium is the most popular methodology in tanneries because it is faster than other processes, involves lower costs, and furnishes leather that is lighter in color and more stable.<sup>7</sup> However, only 60% of the applied chromium is normally taken up by the leather; the excess is discharged as waste into the effluent. Consequently, tannery wastewaters contain high chromium concentrations and elimination of this contaminant is of considerable concern.<sup>8,9</sup> Although Cr(III) is considered essentially immobile

**Received:** February 9, 2012

**Accepted:** April 24, 2012

**Published:** April 24, 2012

in the environment, chromium(VI) is mobile and toxic. Bini et al. have pointed out that chromium can no longer be relegated as a metal restricted to local contamination.<sup>10</sup>

Many processes have been proposed for the removal of heavy metals from contaminated wastewater. Adsorption is considered as the most suitable and economical method for the removal, recovery, and recycling of these ions. In this sense, natural adsorbents such as clays and zeolites are among the most commonly employed materials. Despite the significant advantages of these solids, numerous approaches have been undertaken in order to improve the adsorption properties of these adsorbents concerning heavy metal removal. For example, the adsorptive capacity of adsorbents is often reported to be improved by functionalization of their surfaces with organic ligands, but the access of the heavy metal to the organic ligand is often difficult due to the textural properties of the solid.<sup>11,12</sup> Even though countless adsorbents have been described as low-cost alternatives in the literature, the search for even cheaper and more effective adsorbents is still necessary. The first destination of chromium after its removal via adsorption is its reuse in leather tanning. The adsorbent also needs to be recovered, so that it can be reutilized and the environmental impact generated from this process can be minimized. Another possible application for chromium-containing adsorbents would be their use as catalysts in various reactions of industrial importance, considering the excellent catalytic ability of solids containing this metal.

In this sense, we have recently reported the excellent adsorption properties of takovite–aluminosilicate nanocomposite for removal of Cr(III) ions from aqueous solutions.<sup>13</sup> Takovite is a layered double hydroxide material, with theoretical formula  $[\text{Ni}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$ , which in our case was synthesized by a coprecipitation methodology. As an aluminosilicate phase was also formed during takovite precipitation, this adsorbent can be viewed as a takovite–aluminosilicate nanocomposite. Thus, the above-mentioned chromium adsorption process by takovite will be even more effective if the takovite–chromium solid resulting from the adsorption process can be employed as an effective catalyst, which will be the object of the present work.

The controlled oxidation of alkanes, alkenes, and aromatic hydrocarbons is highly desirable for the conversion of oil derivatives into commercially valuable chemicals.<sup>14</sup> Undoubtedly one of the most common transformations undergone by alkenes is epoxidation. Epoxides are very useful intermediates in the chemical industry and are the starting point for the preparation of various products such as drugs and paints.<sup>15</sup> Cyclohexane oxidation is another important reaction, since it furnishes cyclohexanol and cyclohexanone (mixture known as K–A oil), raw materials for the production of nylon 6 and 6.6. The industrial synthesis of these products is carried out at 150 °C and 1–2 MPa, with homogeneous catalysts (normally Co or Mn salts). Despite these conditions, low cyclohexane conversion of 4% with 70–85% selectivity for cyclohexanol and cyclohexanone is achieved, producing high quantities of waste byproducts.<sup>16</sup>

Over the last years increasing attention has been given to the use of clean technologies employing hydrogen peroxide as oxidant. This compound is a promising oxygen donor because it is relatively cheap and readily available, and also contains a high level of active oxygen (47%). Moreover, only water and oxygen are generated from this oxidant, which should help reduce the costs related to industrial wastewater treatment. On

the other hand, chromium-based catalysts have attracted a lot of interest from numerous catalytic sectors. Common examples are the polymerization reactions making use of Cr/SiO<sub>2</sub> matrices (Phillips catalysts) and the epoxidation reactions utilizing oxides or chromium salen compounds.<sup>17</sup>

In this context, the catalytic efficiency of takovite–chromium catalysts obtained via adsorption of chromium from aqueous solutions by a takovite–aluminosilicate nanocomposite adsorbent is investigated in this work. These catalysts were used in the oxidation of (*Z*)-cyclooctene and cyclohexane by hydrogen peroxide, at room temperature.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of the Takovite–Aluminosilicate Adsorbent.** The preparation of the adsorbent has been reported elsewhere.<sup>18,19</sup> Briefly, it was synthesized by the co-precipitation method, by addition of concentrated ammonia to a mixture of NiCl<sub>2</sub>·6H<sub>2</sub>O, AlCl<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and tetraethylortosilicate (TEOS) in dichloromethane. When pH 11 was reached, the mixture was refluxed at 60 °C for 20 h.

**2.2. Adsorption Experiments.** Chromium adsorption has also been reported elsewhere.<sup>13</sup> Briefly, it was carried out by the batch method, using 0.1 g of adsorbent and 10.0 mL of 2.0, 3.0, 6.0, or 8.0 mM Cr<sup>3+</sup> solutions (prepared by CrCl<sub>3</sub>·6H<sub>2</sub>O dissolution), at 25 °C and for 180 min. The obtained catalysts were denoted T-Cr-2, T-Cr-3, T-Cr-6, and T-Cr-8, respectively, “T” denoting the takovite–aluminosilicate adsorbent, “Cr” indicating that the solid had been in contact with Cr<sup>3+</sup> solutions, and the last number referring to the concentration of such solutions. For comparison, the original takovite adsorbent without adsorbed chromium was utilized as “blank” and named T.

**2.3. Characterization Techniques.** The characterization of the takovite–aluminosilicate adsorbent and of the derived Cr-catalysts<sup>13</sup> has been reported elsewhere. The characterization has now been extended by using the techniques described below.

FT-IR spectra in the 4000–350 cm<sup>-1</sup> range were recorded on a Perkin–Elmer 1730 Infrared Fourier Transform Spectrometer, using the KBr pellet technique. About 1 mg of the sample and 300 mg KBr were employed in the preparation of the pellets.

Electronic spectra of the materials were registered on a Hewlett–Packard 8453 Diode Array UV–Vis spectrophotometer.

Specific surface areas were determined by applying the BET method to the corresponding nitrogen adsorption isotherms, obtained by using a physical adsorption analyzer Micrometrics ASAP 2020. The samples (0.2 g) had been previously degassed for 6 h at room temperature, at a pressure lower than 50 μmHg.

Photoacoustic spectroscopy (PAS) absorption measurements were accomplished on a spectrometer manufactured by Optical Properties Laboratory (Physical Institute of UFBA, Brazil). This instrument bears a halogen lamp (250W/24 V) source, mounted at the focus of a concave mirror that projects the filament image into a collimator slit–convergent lens set, generating a parallel beam. The white or polychromatic beam is sent to the monochromator, which is composed of a grating, convergent lens, collimator and output slit. The monochromatic light that emerges from the collimator is intersected by a chopper–type mechanical modulator (SR540 by Stanford) at a frequency of 24 Hz. The grating angular position is related to the selected wavelength, and it is determined by a stepper motor and controlled by a purchase and control software. At the end of each mechanical step, the analogical information provided by the light sensors and detected by the SR540 lock–in amplifiers (Stanford Research) is acquired and stored by a personal computer. The spectra were collected in the 300–1800 nm range. The detector output signal was applied to a lock–in amplifier that performed detection of the synchronous signal, signal amplification, and noise rejection. For a largely reflective sample, it was possible to increase the sensitivity of the measurement (XS00) by connecting a homemade device able to amplify very low noises, with no compromise of the signal-to-noise ratio. The monochromatic output light had an intrinsic resolution of

1.2 nm or 0.2%, as obtained by the calibration process; the energy resolution was 2.8%.

Differential pulse voltammetry (DPV) measurements were conducted on a potentiostat/galvanostat PARC, model 273. All the experiments were carried out using a conventional three-electrode cell. The takovite–aluminosilicate adsorbent modified graphite electrode with an exposed surface area  $S = 0.152 \text{ cm}^2$  and glassy carbon ( $0.082 \text{ cm}^2$ ) were used as the working electrodes. The modified working electrode consisted of the PVC body containing a graphite disk, which supported the carbon paste. The latter was prepared by mixing high-purity graphite (Fisher Scientific) and the adsorbent material in a 9:1.5 (w/w) ratio with a drop of mineral oil. Ag/AgCl was employed as the reference electrode, and platinum wire functioned as the auxiliary electrode. All the measurements were performed under high purity argon. A HCl/KCl solution (pH = 0) or buffer solutions with pH 3 or 5 served as the supporting electrolyte.

#### 2.4. Catalytic Performance. 2.4.1. (Z)-Cyclooctene Oxidation.

The catalytic performance of the takovite–chromium catalysts was tested in the epoxidation of (Z)-cyclooctene by hydrogen peroxide. For this purpose, 1.28 mmol 70 wt %  $\text{H}_2\text{O}_2$  (concentration confirmed by iodometric titration), used as received, was added to a 2  $\text{cm}^3$  vial sealed with a Teflon-coated silicone septum containing one of the T-Cr catalysts (10 mg) suspended in 1  $\text{cm}^3$  of a 1:1 1,2-dichloroethane/ acetonitrile mixture, (Z)-cyclooctene (previously purified on an alumina column) as substrate (1.15 mmol), and di-*n*-butyl ether as internal standard (10  $\mu\text{L}$ ).

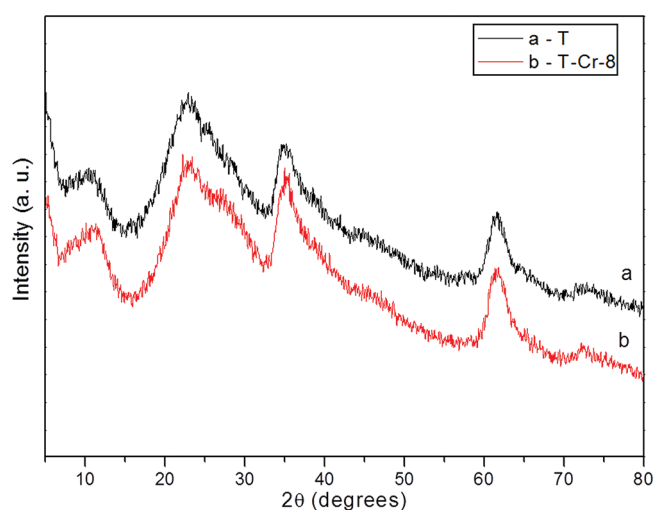
**2.4.2. Cyclohexane Oxidation.** The catalytic activity and selectivity were evaluated by addition of different molar ratios of active sites, oxidant, and substrate. For this purpose, in the first conditions considered (active site/substrate/oxidant = 1:100:500), 0.047  $\text{cm}^3$  of 70 wt %  $\text{H}_2\text{O}_2$  (used as received, concentration confirmed by iodometric titration, 1.372 mmol) were added to a 2  $\text{cm}^3$  vial sealed with a Teflon-coated silicone septum containing one of the T-Cr-8 catalyst (10 mg) suspended in 1.12  $\text{cm}^3$  of a 1:1 1,2-dichloroethane/ acetonitrile mixture, 0.03  $\text{cm}^3$  (0.277 mmol) of cyclohexane, previously purified on an alumina column as substrate, and 10  $\mu\text{L}$  (5.89 mmol) of di-*n*-butyl ether as internal standard. In the second experiment, the molar ratio of the reactants was 1:100:1000; only the volume of the oxidant was changed to 0.094  $\text{cm}^3$  (2.744 mmol).

All the reactions were conducted at atmospheric pressure and room temperature, and monitored by gas chromatography (HP 6890, equipped with a hydrogen flame ionization detector, HP-INNOWax capillary column with a length of 30 m and internal diameter of 0.25  $\mu\text{m}$ ). The conversion was determined by comparison with pure compounds, using calibration curves and di-*n*-butyl ether as internal standard.

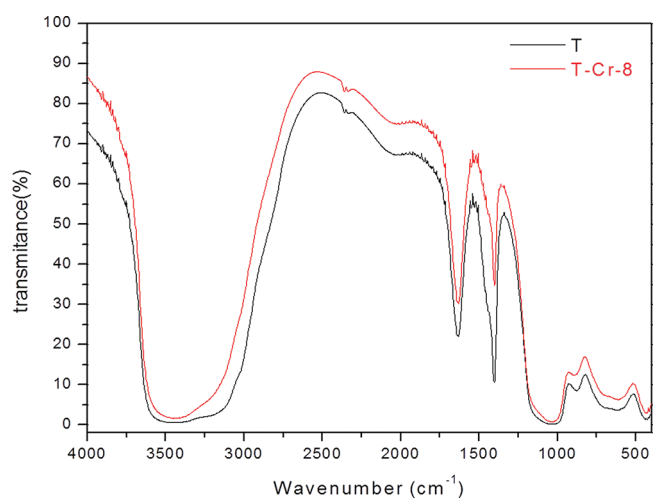
### 3. RESULTS AND DISCUSSION

**3.1. Characterization of the Catalysts.** The original adsorbent consists of a mixture of Ni–Al hydrotalcite, namely takovite, and an amorphous aluminosilicate phase. Takovite has a basal spacing of 7.76 Å, with low crystallinity and carbonate and chloride as interlayer anions. After  $\text{Cr}^{3+}$  adsorption, the basal spacing remains at 7.76 Å, also without significant changes in the crystallinity of the solid (Figure 1).

The FT-IR spectrum of the original solid (Figure 2) is a combination of those of its two constituents, with bands corresponding to hydroxyl groups and water (3500 and 1635  $\text{cm}^{-1}$ ), carbonate anions (1409 and 877  $\text{cm}^{-1}$ ), Si–O groups (1053  $\text{cm}^{-1}$ ) and Ni–O and Al–O bonds at lower wavenumbers. After  $\text{Cr}^{3+}$  adsorption, there is a significant variation in the form and position of the band due to carbonate vibration, which is shifted to 1395  $\text{cm}^{-1}$ . A similar change, although much less evident, can also be observed for the  $\nu_2$  vibration mode of this anion, which shifts to 888  $\text{cm}^{-1}$  after  $\text{Cr}^{3+}$  adsorption. This strongly suggests an interaction between carbonate and  $\text{Cr}^{3+}$ ;



**Figure 1.** X-ray powder diffraction patterns of takovite-aluminosilicate solid before (a) and after (b) adsorption of  $\text{Cr}^{3+}$ .

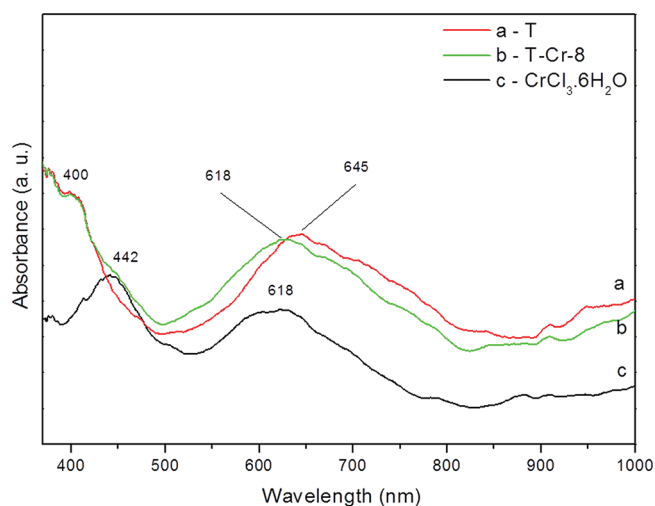


**Figure 2.** Infrared spectra of the solids takovite-aluminosilicate and T-Cr-8 catalysts.

the cations may be coordinated to the anions located in the interlayer region of takovite.

The UV–visible photoacoustic spectrum of the solid  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  presents the typical absorbance properties of  $\text{Cr}^{3+}$  cations in an octahedral environment, with two intense d–d transition bands at 442 and 618 nm (Figure 3). It is well-known that these bands, designated  $\nu_2$  and  $\nu_1$ , correspond to  ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{F})$  and  ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_2\text{g}(\text{F})$  transitions. Moreover, the  $\nu_4$  band, corresponding to the spin–forbidden  ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^2\text{E}_\text{g}$  transition and usually called ruby line, is observed as a small shoulder at 695 nm. The spectrum of takovite displays a band at 400 nm, typical of the ligand–to–metal charge transfer of Ni–O bonds in takovite, although it may also be compatible with the  $\nu_2$  ( ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{P})$ ) transition of  $\text{Ni}^{2+}$  cations in octahedral environment. The most intense band exhibited by this solid is the one centered at 645 nm, corresponding to the  $\nu_4$ ,  ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{F})$ ,  $\text{Ni}^{2+}$  transition. The spectrum of the takovite– $\text{Cr}^{3+}$  solid has a band at 400 nm, which is very similar to that observed in the case of takovite, confirming that it corresponds to  $\text{Ni}^{2+}$  charge transfer (it may be considered that this solid is mainly composed of takovite, and that the amount of  $\text{Cr}^{3+}$  is low). At the same time,



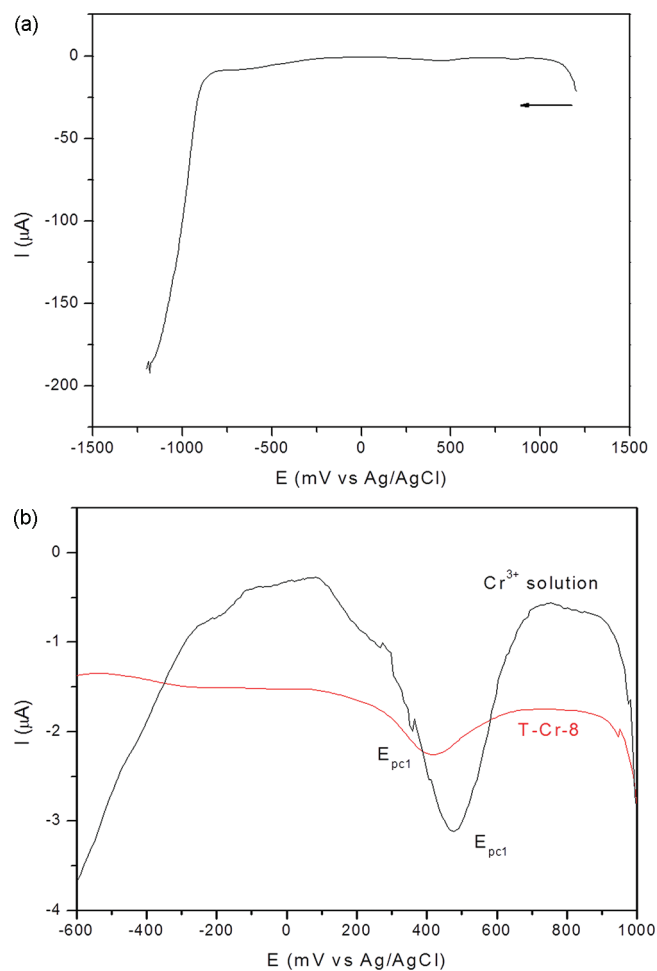


**Figure 3.** UV–visible photoacoustic spectroscopy of the solids takovite, T-Cr-8 catalyst and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .

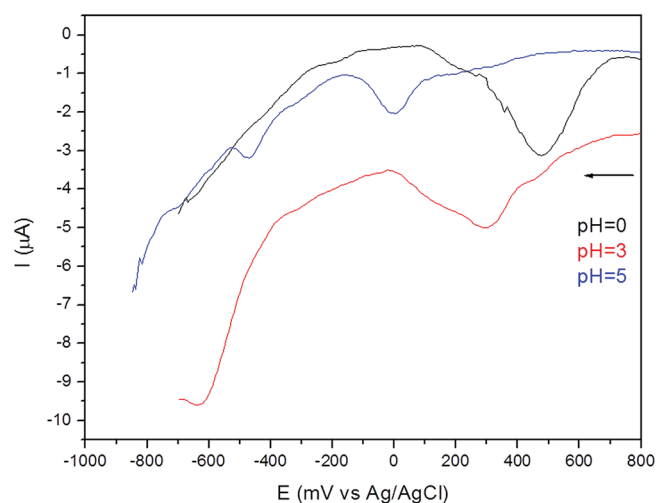
a shoulder at 442 nm can be verified. The decomposition of the spectrum reveals a large band at 420 nm, close to the bands relative to  $\text{Cr}^{3+}$ - and  $\text{Ni}^{2+}$ -charge transfer, so it can be due to a contribution of both of them. The main band in the spectrum is located at 618 nm, which is in excellent agreement with the spectrum of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ . This clearly suggests that adsorbed  $\text{Cr}^{3+}$  cations reach an octahedral environment in the solid, which probably involves coordination with carbonate and hydroxyl anions and water molecules in the interlayer region of takovite. It is noticeable that in this solid the main absorption band at 618 nm is situated at the position characteristic of  $\text{Cr}^{3+}$  transition and is clearly shifted from the position of the  $\text{Ni}^{2+}$  transition, even though  $\text{Ni}^{2+}$  is the major transition cation and  $\text{Cr}^{3+}$  is the minor. This can also be related to changes in the  $\text{Ni}^{2+}$  environment taking place during the adsorption process. Indeed, the takovite suspension in the aqueous solution may promote the substitution of oxo by hydroxyl anions in the  $\text{Ni}^{2+}$  coordination sphere, thus making the band to shift to higher energy.

Figure 4 shows the differential pulse voltammograms (PDV) of the T-Cr-8 electrode in aqueous solution at pH = 0. The voltammetric curve displays a cathodic current peak around +420 mV ( $E_{\text{pc1}}$ ) with the corresponding anodic current peak (not shown) vs Ag/AgCl. This current peak does not appear in original takovite and is shifted if compared with the process observed in a  $\text{Cr}^{3+}$  solution. These results prove that  $E_{\text{pc1}}$  wave is due to  $\text{Cr}^{3+}$ , and is probably a result of the  $\text{Cr}(\text{IV})/\text{Cr}(\text{III})$  redox process. Additionally, in analogy with the PA spectrum and infrared spectroscopy results, it can be hypothesized that adsorbed  $\text{Cr}^{3+}$  interacts with carbonate groups present in the takovite.

Subsequently, we analyzed whether the cathodic peak value is pH-dependent. The PDV of T-Cr-8 was recorded in aqueous solution at pH 0, 3, and 5 (Figure 5). The shift in the potential values ( $E_{\text{pc1}}$ ) clearly suggests that the interaction between  $\text{Cr}^{3+}$  ions and takovite is pH-dependent, which is consistent with the hydrolysis reaction of this ion. As indicated before,  $\text{Cr}^{3+}$  adsorbed by takovite may be coordinated to water, hydroxyl, and carbonate species, thus the changes in pH strongly affect both the stability of the carbonate anions and the formation of  $[\text{Cr}(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(3-n)+}$  cations. Therefore, in very acidic conditions (pH = 0), in which chromium may be in a form very



**Figure 4.** Differential pulse voltammogram of T-Cr-8 and original takovite aluminosilicate (inset). Scan rate ( $\nu$ ) =  $100 \text{ mV s}^{-1}$ , in aqueous solution at pH = 0.

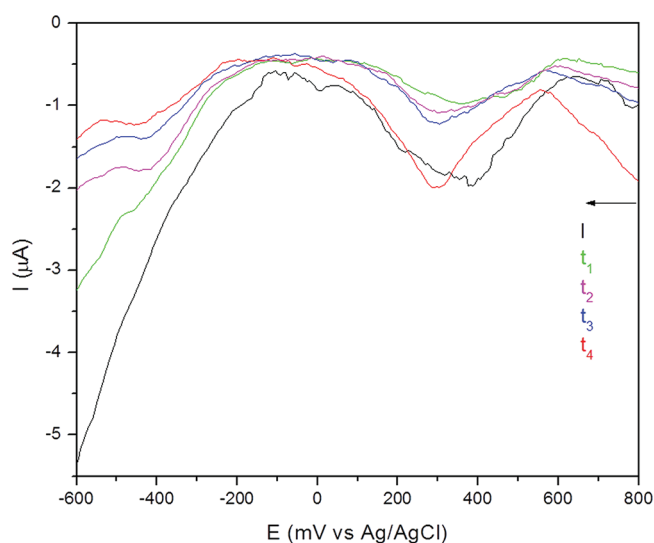


**Figure 5.** Differential pulse voltammogram of T-Cr-8 solid. Scan rate ( $\nu$ ) =  $100 \text{ mV s}^{-1}$ . In aqueous solution, at pH = 0, 3, and 5.

close to  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , the more positive  $E_{\text{pc1}}$  value illustrates that  $\text{Cr}^{3+}$  is more stabilized than at higher pH values (3 and 5). Chromium may be leached from the solid at acidic pH 0, at which the stabilization of the 3+ oxidation state is higher than

that of the 4+ state. This favors the reduced form, in agreement with the observed results.

To obtain information about the adsorbent properties of takovite with respect to chromium ions, PDV was recorded at different times. To this end, a takovite–electrode was placed in  $10^{-3}$  M  $\text{Cr}^{3+}$  solutions at pH = 3 (Figure 6). The  $t_1$  PDV



**Figure 6.** Differential pulse voltammogram of takovite-electrode in  $\text{Cr}^{3+}$  aqueous solution pH = 3.  $I$  = initial,  $t_1$  = 2 min,  $t_2$  = 10 min,  $t_3$  = 15 min, and  $t_4$  = 20 min. Scan rate ( $\nu$ ) =  $100 \text{ mV s}^{-1}$ .

illustrated a minor intensity current compared with curve  $t_2$ . Thereafter, the current increased and then remained constant. These results clearly demonstrate an interaction between the  $\text{Cr}^{3+}$  cations and takovite.

The initial voltammogram, obtained immediately after contact between the adsorbent and the  $\text{Cr}^{3+}$  solution (Initial), revealed a potential of +379 mV, which decreased with increasing contact time. This reduction is clearly visible, especially after 10 min of contact. In other words, a longer contact time prompts a rise in current (curve  $t_4$ ). The final potential was +295 mV. This clearly proves a progressive stabilization of the  $\text{Cr}^{3+}$  cations fixed by the adsorbent matrix.

The takovite material has a large surface area,  $296 \text{ m}^2/\text{g}$ , and its total pore volume is also high,  $0.608 \text{ cm}^3/\text{g}$ . Adsorption studies have indicated that this solid is a good adsorbent for  $\text{Cr}^{3+}$  ions. The equilibrium capacity under the conditions employed in the kinetic experiments was evaluated as being  $250 \mu\text{mol g}^{-1}$ ; saturation values were only reached for the most concentrated metal solutions. The adsorption increases with time, and the equilibrium is achieved after 180 min of contact between takovite and the  $\text{Cr}^{3+}$  ions.<sup>13</sup> Incorporation of  $\text{Cr}^{3+}$  into the adsorbent does not produce significant changes in the adsorbent's morphology. In other words, it is possible to prepare a good adsorbent of heavy metals without previous functionalization of the solid with organic ligands. The fact that the  $\text{Cr}^{3+}$  ions adsorb onto the surface is extremely interesting. Metal access to the clay is good, and the solid has large loading capacity and leads to high metal–adsorbent bond constants. In fact, the  $\text{Cr}^{3+}$  ions can be adsorbed onto the takovite interlayer space, which contains carbonate anions, and onto the surface, binding to Ni–O or Ni–OH, so it is extremely interesting to carry out catalytic studies because the good access of the metal, the substrate and the oxidant to the clay interlayer may

promote high substrate conversion and product diffusion. Differential pulse voltammetry was employed in pursuit of additional information about the adsorbed  $\text{Cr}^{3+}$  ions. Taking the present results into account, it is reasonable to consider that the change in the intensity and position of the cathodic wave illustrated in Figure 6 confirms the  $\text{Cr}^{3+}$  incorporation into the takovite materials. Hence, it can be said that the takovite prepared herein performs extremely well as adsorbent, and that the obtained Cr-solids can be potentially applicable in green chemistry, the reason why they have been tested as oxidation catalysts.

### 3.2. Application of the Takovite– $\text{Cr}^{3+}$ Solids As Catalyst.

Table 1 lists the epoxide yields obtained when the

**Table 1.** Conversion to (Z)-Cyclooctenoxide (%) from the Oxidation of Z-Cyclooctene by  $\text{H}_2\text{O}_2$ <sup>a</sup>

catalyst	$\text{Cr}^{3+}$ amount (mmol) <sup>b</sup>	turnover (TON)	conversion (%)
T			25
T-Cr-2	$2.72 \times 10^{-5}$	29590	70
T-Cr-3	$9.30 \times 10^{-5}$	9270	75
T-Cr-6	$1.65 \times 10^{-4}$	5580	80
T-Cr-8	$2.75 \times 10^{-4}$	3770	90
FeTFPP-Al	$2.07 \times 10^{-4}$	6189	100

<sup>a</sup>An iron(III)-porphyrin (FeTFPP-A) was also tested as catalyst for comparison. <sup>b</sup>Millimoles of  $\text{Cr}^{3+}$  in 10 mg of takovite solid catalyst.

$\text{Cr}^{3+}$ -containing solids were used as catalysts in the epoxidation of Z-cyclooctene by  $\text{H}_2\text{O}_2$ , leading to epoxide yields between 70–90%. A control reaction carried out using the original takovite (T) without adsorbed  $\text{Cr}^{3+}$  furnished epoxide yields of only 20%. This demonstrates that the presence of  $\text{Cr}^{3+}$  is essential for the formation of the active species responsible for the oxygen transfer from the oxidant to the substrate. All the  $\text{Cr}^{3+}$  solids utilized in this work resulted in high selectivity, being (Z)-cyclooctenoxide the only reaction product.

The selectivity toward the epoxide reported here is higher than the values found in the literature; for instance, Lu et al.<sup>20</sup> used  $\text{CrO}_2\text{Cl}_2$  as catalyst/oxidant for Z-cyclooctene oxidation and achieved low epoxide yields (~3%) as well as various undesired byproducts.<sup>20</sup> Koshi et al. obtained epoxide yields around 70% by employing Cr–salen compounds as catalysts for (Z)-cyclooctene oxidation,<sup>21</sup> but this system required the use of a cocatalyst (pyridine) and the oxidant used in this case was iodosylbenzene, which is environmentally very harmful. The role of pyridine in this system was to promote the formation of the active metal–oxo species.

The catalytic activity increased with the amount of adsorbed  $\text{Cr}^{3+}$ , and a Z-cyclooctenoxide yield close to 90% was achieved with the T-Cr-8 solid. The turnover number (TON) for the Z-cyclooctene oxidation reaction was calculated to compare the activities (see Table 1). In the case of heterogeneous catalytic processes, TON is a description of the number of active sites, so measuring the activity of a solid catalyst is rendered difficult because the substrate can easily generate new active sites on the catalyst particle, not to mention the possible changes in the surface during the adsorption/desorption process.<sup>22</sup> On the basis of the results presented in Table 1, it can be noted that the generated products and the remaining reactants can compete for active sites as the reactants are consumed. This fact accounts for the lower TON values obtained at higher concentrations of  $\text{Cr}^{3+}$  ions. The large number of active sites

can be inactivated by the generated products and remaining reactants, thereby resulting in diminished TON values.<sup>23</sup>

The UV–vis spectra of the reaction supernatants recovered after the oxidation reactions revealed that they contained no chromium ions in any oxidation state, thereby demonstrating that there was no metal leaching from the support during the catalytic reaction. To prove that the catalytic reaction was truly heterogeneous, the reaction supernatant was filtered off at the end of the oxidation and more oxidant was added. Then, the supernatant containing extra oxidant was left to react in a similar way to the oxidation carried out using the solid catalyst, and this was monitored over 48 h. No product from *Z*-cyclooctene oxidation was formed, proving that the solid catalyst genuinely played a crucial role in this process. This was expected since  $\text{Cr}^{3+}$  is considered to be a hard acid according to Pearson's classification,<sup>24</sup> so it easily coordinates with oxygen, a hard base. Apart from presenting great affinity for oxygen binding, chromium is also highly labile, which is ideal for the formation of a good catalytic system. This fact might be due to the possibility of Cr ions forming different complexes with Lewis bases such as carbonate, water, peroxide and also with substrates such as *cis*-cyclooctene and cyclohexane. The formation of the labile  $\text{Cr}^{\text{IV}}=\text{O}$  active species is probably favored during the reactions, without its leaching from the takovite matrix. The electron free pair from oxygen of carbonate anions from takovite aluminosilicate is highly adapted to favor the formation of high-valent oxidation states of a metal center, still keeping a sufficient lability of the metal–oxygen bond in order to obtain a facile oxygen atom transfer to various substrates. However the stability of these high-valent metal species is highly dependent of the nature of the ligands.

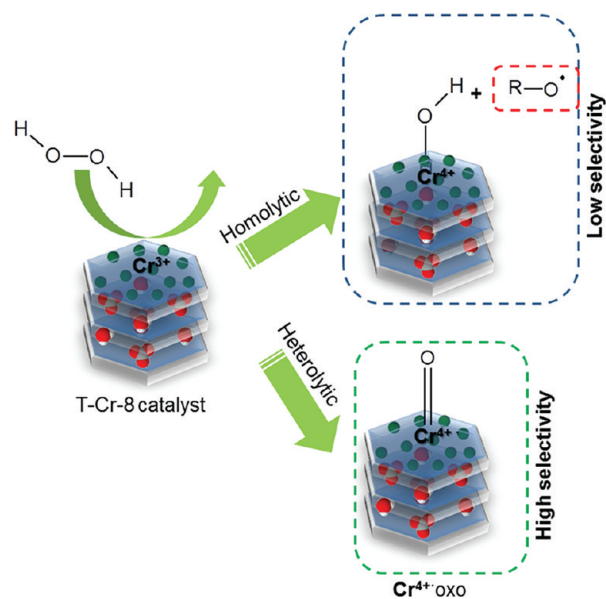
The mechanisms through which transition metals activate C–H bonds are still controversial. These mechanisms can be divided into three categories: the first involves a metal–peroxo species, the second includes a metal–oxo species, and the third involves radical species. There is a literature consensus that metals like Mo, V, and Ti catalyze epoxidation reactions via peroxo active species, while metals such as Cr and Ru make use of metal–oxo species.

A homolytic peroxide cleavage leading to radical species may occur in the presence of oxidants such as hydrogen peroxide (Figure 7). These radical species may cause considerable loss of selectivity.

The high-valent metal–oxo species is well established for systems involving iron(III)–porphyrins (FePs) as catalysts and iodosylbenzene as oxidant. In this case, the epoxide is formed via formation of an active ferryl radical species, as depicted in Figure 7.

Because most of the knowledge about the high valent metal–oxo species is derived from studies involving enzyme model systems such as those employing synthetic metalloporphyrins, we compared the results obtained with takovite–Cr solids with those achieved with the second generation iron(III)porphyrin  $\text{Fe}(\text{TFPP})^+$  encapsulated in an alumina matrix, designated FeTFPP-A. In the literature, this FeP has been extensively used as catalyst in *Z*-cyclooctene oxidation by iodosylbenzene, which has proven to be a system that leads to alkene epoxidation through an iron–oxo high valent species.<sup>25</sup>

Catalytic yields obtained with the T–Cr system were similar to those achieved with the FeTFPP-A system. However, in the case of the FeP system, the catalyst concentration on the support was 2.2% (22 mg of FeP in 1 g of alumina), which is almost 5-fold the concentration of chromium on takovite; that



**Figure 7.** Homolytic and heterolytic peroxide cleavage in presence of takovite solid catalysts.

is, 0.4%. Another advantage of the T–Cr systems is that they are cheaper than FePs, not to mention that the latter demand arduous purification procedures and the use of chlorinated solvents in their syntheses.

Although our catalytic studies are still preliminary, a possible reaction mechanism can be proposed. As reported previously by us,<sup>19</sup> before chromium adsorption original takovite furnishes an epoxide yield of 20%. In that work, we had observed that two oxidation mechanisms were taking place, namely the heterolytic and the homolytic processes, and that there was a competition between them. To find out whether both these mechanisms still occurred in the presence of  $\text{Cr}^{3+}$ , the oxidation reaction was carried out using the solid with the highest  $\text{Cr}^{3+}$  content (T–Cr-8) in the presence of the radical traps *tert*-butyl alcohol and quinine. The cyclooctenoxide yield was the same as that obtained in the absence of the alcohol, so the presence of radical species in this system can be ruled out. Interestingly, the homolytic mechanism does not take place in the presence of chromium; only the heterolytic one occurs.

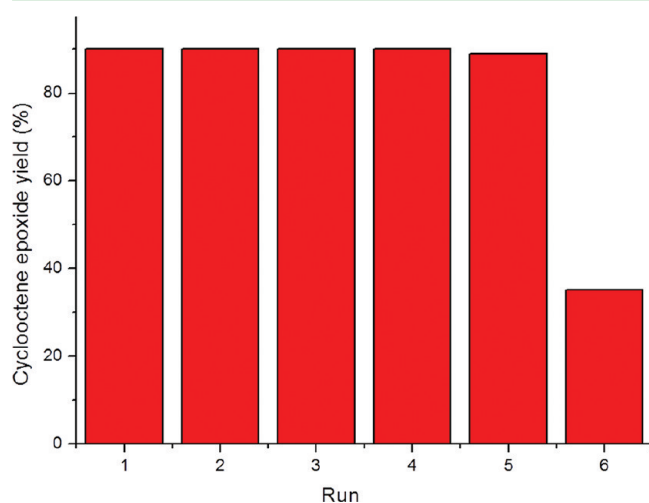
On the basis of the high selectivity for the epoxide, the absence of radical mechanisms, and the cyclooctenoxide yields similar to those obtained with the FeP system, we propose that the oxidation reaction mechanism in the presence of  $\text{Cr}^{3+}$  ions adsorbed on takovite occurs in a way similar to that proposed by Lu et al.<sup>20</sup> for Cr catalysts and by Caetano et al.<sup>26</sup> for Co catalysts; that is, via formation of a high valent metal–oxo active species.

Therefore, epoxidation should occur in two steps. First, the active species  $\text{Cr}^{\text{IV}}=\text{O}$  should be formed via a one-electron oxidation of the  $\text{Cr}^{3+}$  ions by hydrogen peroxide. Then, the  $\text{Cr}^{\text{IV}}=\text{O}$  species should transfer the oxygen atom to the  $\text{C}=\text{C}$  bond of the substrate, thus generating the epoxide.

Another interesting observation is that these yields were reached after 24 h of reaction. Reactions of this type generally require a longer time interval for diffusion of the product. This faster reaction in our case can be attributed to the adsorption of the  $\text{Cr}^{3+}$  ions on the surface of the matrix, as observed by TEM. This should facilitate the access of both the oxidant and the

substrate to the chromium ions, and the diffusion of the product back to the solution.

Having in mind that catalysts in general have become cheaper and greener due to the utilization of recyclable heterogeneous catalysts and having green chemistry as an objective, the recyclability of such materials was tested. The results for the reuse experiments employing hydrogen peroxide as oxidant and the T-Cr-8 catalyst are given in Figure 8. To this



**Figure 8.** Catalytic activity of the T-Cr-8 catalyst in six consecutive runs.

end, the catalyst was separated from the reaction mixture after each experiment by simple filtration and dried before utilization in a subsequent run. The catalyst could be reused for five consecutive runs without loss in yield. After the sixth reuse, the epoxide yield decreased to 35%. It may be remarked here that all the reactions were conducted at room temperature.

To confirm the diversity of the as-prepared catalysts, the performance of T-Cr-8 in the oxidation of cyclohexane by hydrogen peroxide was tested at room temperature and atmospheric pressure (Table 2). Besides its industrial

**Table 2.** Conversion of Cyclohexane to Cyclohexanol (OL, %) and Cyclohexanone (ONE, %) Using  $\text{H}_2\text{O}_2$  as Oxygen Donor and T-Cr-8 as Catalyst

catalyst	$\text{Cr}^{3+}$ amount (mmol)	turnover (TON)	conversion (%)		
			OL	ONE	total
T (1:100:500) <sup>a</sup>			0	0	0
T-Cr-8 (1:100:500) <sup>a</sup>	$2.75 \times 10^{-4}$	8198	4	5	9
T (1:100:1000) <sup>a</sup>			0	0	0
T-Cr-8 (1:100:1000) <sup>a</sup>	$2.75 \times 10^{-4}$	15038	8	10	18

<sup>a</sup>Reactant ratio (active site:substrate:oxidant).

importance, this substrate is less reactive than alkenes, so it is ideal to prove the efficiency and moreover the selectivity of a given catalyst. Several works in the literature have reported the use of chromium catalysts in cyclohexane oxidation,<sup>27,28</sup> but some of them displayed low activity and there was a leaching of the metal from the supports. Great advances have been made by supporting chromium on mesoporous matrices; however, these reactions generally demand drastic conditions such as

elevated temperature (100 °C) and long reaction times (over 12 h), making their industrial use impractical.

Results from cyclohexane oxidation reactions using the T-Cr-8 catalyst are summarized in Table 2. The materials catalyzed the oxidation of the cyclohexane saturated C–H bonds, giving 100% selectivity toward cyclohexanol and cyclohexanone; no other by-product was observed.

Control reactions were conducted in the following conditions: absence of chromium (takovite was employed); absence of oxidant; and absence of solvent. Neither of the control reactions afforded any product yield. The absence of oxidized products from cyclohexane in the case of the reaction using takovite blank evidence that the  $\text{Cr}^{3+}$  ions play an important role in mediating oxygen transfer from the oxidant to the substrate, being the active catalytic sites in the oxidation reaction.

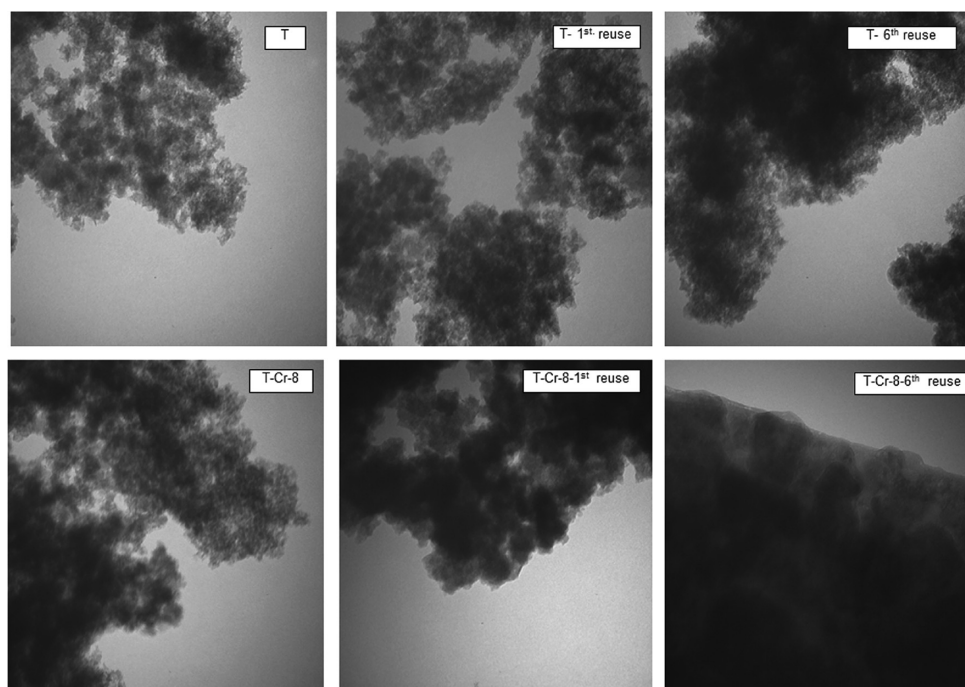
The oxidation of several organic substrates such as cyclohexane is known to depend on the nature of the solvent, because in some cases the solvent can interact with the active sites of the catalysts.<sup>29</sup> Several literature works reporting on the use of Ce–MCM–41 or Ti–zeolite have described that in the presence of acetic acid the yields of oxidized products from cyclohexane were improved. This was attributed to the fact that, apart from being very good for medium homogeneity, this acid also acts as a good oxidizing agent. Using titanium silicates matrix as catalysts, Sooknoi et al.<sup>29</sup> had observed that acetic acid could be oxidized to peracetic acid, which in turn would form a titanium–peracetic hydrophobic complex that interacts with cyclohexane better. Some articles have also stated that the decomposition of hydrogen peroxide is faster in organic solvents like acetonitrile. For this reason, we investigated this reaction in acetonitrile and acetic acid media. In our case, the use of acetic acid did not raise the catalytic yields. Indeed, when this solvent was employed in our work, the maximum conversion was only 1% ketone. Table 2 also shows that when the catalyst/oxidant molar ratio was increased (1: 1000), the materials were significantly more active compared to the 1:500 ratio. This result can be attributed to the decomposition of hydrogen peroxide, which was minimized when more oxidant was employed. In both conditions studied herein, it was observed that the catalytic oxidation of cyclohexane yielded cyclohexanone as the main product, and the same product distribution (ketone/alcohol ~1.2) was achieved in both cases. It is also noteworthy that, in spite of the presence of  $\text{Cr}^{3+}$  ions, no products from the auto-oxidation of cyclohexane were detected, for example, cyclohexyl hydroperoxide.

Several literature works have reported that cyclohexanone is produced from cyclohexanol overoxidation. To verify whether this was the case in our system, the oxidation reaction was performed using cyclohexanol, and not cyclohexane, as substrate. There was no formation of cyclohexanone in significant amounts, so formation of the ketone from alcohol overoxidation was ruled out; cyclohexanone must have been formed by direct cyclohexane oxidation.

It is worth highlighting that there was no leaching of the  $\text{Cr}^{3+}$  ion from the support in any of the conditions studied herein, demonstrating that the catalysis was typically heterogeneous.

Radical species can be responsible for cyclohexane oxidation when catalyzed by metal ions. To verify whether radical mechanisms were involved in the case of the T-Cr-8 catalyst, the reactions were also accomplished in the presence of the radical scavenger quinine. The latter did not diminish the product yields, so the involvement of radical species as the





**Figure 9.** Transmission electron micrographs of the takovite aluminosilicate materials before and after catalysis oxidation reactions with magnifications of 25000 $\times$ .

oxidant agent was ruled out. The reaction was also performed in the absence of oxygen, and no decrease in product formation was detected, thereby confirming that the formation of cyclohexanol and cyclohexanone was not due to cyclohexane or cyclohexanol auto-oxidation. This corroborates the assumption that the active species is the metal-oxo intermediate.

TEM pictures of the takovite-aluminosilicate are displayed in Figure 9. Some platelets embedded in finely powdered matrix are observed in all the samples. Small grains are separated from the layers, which decreases the structural order characteristic of the amorphous nature of the matrix as previously shown in XRD patterns.

TEM pictures of the catalysts also provided some evidence related to the decrease in the catalytic activity after the oxidation reactions. The morphologies of T and T-Cr-8 changed drastically after the sixth reuse of the catalysts, suggesting blockage of porous structure and formation of larger particles, with lower surface area. The blockage of porous structure and densification of takovite-aluminosilicate layers explain the decrease in the catalytic activity of the solids reported in this work and also of other catalysts reported recently.<sup>25,26</sup>

#### 4. CONCLUSIONS

A synthetic material with the main features of takovite and an amorphous aluminosilicate was prepared by means of a simple, inexpensive procedure. This material displayed very promising environmental applications since it can be employed to adsorb chromium from industrial effluents and the resulting chromium-containing solid can act as a potential catalyst for hydrocarbon oxidation by the environmentally friendly oxidant hydrogen peroxide. Although voltammetric studies revealed the redox ability of the chromium ion present in the takovite matrix, this metal ion was not oxidized during the oxidation reactions, and it did not leach from the support. Thus, a novel

catalytic system has been designed by adsorption of the Cr<sup>3+</sup> employed in tanneries.

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##### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work has been carried out in the frame of a Spain-Brazil Interuniversity Cooperation Grant, financed by MEC (PHB2011-0164-PC) and CAPES (267/12). Spanish authors thank additional financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (EDRF) through project MAT2010-21177-C02, and Junta de Castilla y León (SA009A11-2). The Brazilian group thanks the support from Brazilian Research funding agencies FAPESP, CAPES, CNPq, and Peróxidos do Brasil (Solvay) is acknowledged for supplying the 70 wt.% aqueous hydrogen peroxide solution.

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